Dynamics of Supercritical Water (INTERFACE SCIENCE-Solutions and Interfaces)

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Dynamics of supercritical water

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The rotational dynamics of water in super- and subcritical conditions is investigated by measuring the spin-lattice relaxation time T_1 of heavy water (D_2O). The experimentally determined T_1 is shown to be governed by the quadrupolar relaxation mechanism even in the supercritical conditions and to provide the second-order reorientational correlation time τ_{2R} of the O-D axis of a single water molecule. It is then found that while τ_{2R} decreases rapidly with the temperature on the liquid branch of the saturation curve, it remains on the order of several tens of femtoseconds when the density is varied up to twice the critical at a fixed supercritical temperature of 400 ºC. The comparison of τ_{2R} with the angular momentum correlation time shows that the rotational dynamics is not diffusive in supercritical water. The dependence of τ_{2R} on the hydrogen bonding state is also examined in combination with molecular dynamics simulations, and the effect of the hydrogen bonding on the rotational dynamics in supercritical water is found to be weaker than but to be on the same order of magnitude as that in ambient water on the relative scale.

Keywords : supercritical water / rotational dynamics / NMR / inertial effect / hydrogen bonding

Supercritical water receives much attention recently as a novel and clean medium for chemical processes of environmental and industrial importance. The rate of a chemical process in a fluid medium is determined by the thermodynamics and dynamics of hydration of the chemical species involved in the process. Although the overall behavior of a chemical reaction is governed by the free energy profile along the reaction coordinate, the dynamics of hydration often plays an important role in determining the reaction rate constant and is indispensable for a molecular description of the rate constant. The dynamics of supercritical hydration is inseparably related to the dynamical structure of pure solvent water at the supercritical state. Thus, in order to establish the molecular picture of the hydration dynamics in supercritical water, it is essential to characterize the dynamics of supercritical water as a pure solvent. In this work, we determine the reorientational correlation time of a single water molecule in supercritical heavy water (D_2O) by measuring the deuteron NMR spin-lattice relaxation time. We show that the deuteron spin-lattice relaxation time of supercritical heavy water is governed by the quadrupolar mechanism and provides information about the motion of a single water molecule in the configuration space.

In order to realize a supercritical state of heavy water (D_2O), the capillary method was employed. In this method, water is confined in a sealed capillary made of quartz and the capillary is placed in an NMR sample tube. The content of water in the capillary uniquely determines the density at supercritical conditions. The density of supercritical heavy water can be conveniently expressed by the packing fraction, which is defined as the ratio of the (liquid) water volume in the capillary to the total volume of the capillary at room temperature. When the packing frac-

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Scope of research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.

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tion is ρ, the density of heavy water at a supercritical temperature is 1.1ρ g/cm^3, provided that the liquid density is 1.1 g/cm^3 at room temperature. The packing fractions examined in the present work are ρ = +0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 with errors of less than 0.03. The expression ρ = +0.0 means that the packing fraction is smaller than 0.02, though water is definitely present in the capillary. We adopt this expression for the lowest packing fraction since it is not possible in our capillary apparatus to identify ρ precisely when $\rho < 0.02$. Actually, it is sufficient for the following discussion simply to specify that the lowest ρ examined is certainly smaller than 0.1.

The T_1 was determined by the inversion recovery method, and it is related to the reorientational correlation time τ_{2R} of a single water molecule through

$$\frac{1}{T_1} = \frac{3\pi^2}{2}\left(\frac{e^2Qq}{h}\right)^2 \tau_{2R} \qquad (1)$$

where e^2Qq/h is the quadrupolar coupling constant (QCC) which represents the interaction between the quadrupole moment of the D nucleus (eQ) and the electric field gradient at the nucleus (eq). In Fig. 1, we show τ_{2R} as a function of the density ρ over the thermodynamic states examined in the present work. In this figure, the QCC value adopted in Eq. (1) is the ambient liquid phase value of 256 kHz when $\rho > 0.6$ and the system is on the liquid branch of the saturation curve. At the supercritical states with $\rho \le 0.6$, τ_{2R} shown in Fig. 1 is determined through Eq. (1) by assuming that the deviation of the QCC value at a given thermodynamic state from that at the dilute gas state is proportional to the corresponding deviation of the average dipole moment of a water molecule calculated from computer simulations of the TIP4P-FQ model. It is seen that τ_{2R} decreases rapidly with the temperature on the liquid branch of the saturation curve. While the reorientational relaxation proceeds on the order of picosecond in ambient water, it is on the order of several tens of femtoseconds when a supercritical state is realized. At a fixed supercritical temperature of 400 ºC, τ_{2R} is between 45 and 80 fs at the densities from ρ = 0.1 to 0.6. When the chemical shift δ is concerned in the supercritical conditions, it was found that the strength of the density dependence expressed as $\rho\partial\delta/\partial\rho$ is comparable to δ itself.

For the reorientational correlation time τ_{2R}, in contrast, Fig. 1 shows that τ_{2R} changes only by ~30% in response to the density variation from ρ = 0.1 to 0.6 at a fixed temperature of 400 ºC. This shows that the rotational dynamics reflects only partially the change in the state of the hydrogen bonding caused by the density variation. When the intermolecular interaction is absent, τ_{2R} is to diverge due to the conservation of angular momentum. Figure 1 then shows that the intermolecular interaction is effective when the density is above ~1/3 of the critical.

In order to closely see the effect of the hydrogen bonding state on the rotational dynamics, we examine the dependence of τ_{2R} on the number N_{HB} of hydrogen bonds by using the molecular dynamics simulations. It was then observed that the absolute change in τ_{2R} against the variation of N_{HB} is larger by orders of magnitude at the ambient state than at the supercritical states. On the other hand, the relative change at the supercritical states is on the average ~2/3 of that at the ambient state. When seen on the relative scale, therefore, the dependence of the rotational dynamics on the hydrogen bonding state in supercritical water is weaker than but is on the same order of magnitude as that in ambient water. According to Fig. 1 and the number N_{HB} of hydrogen bonds determined from the chemical shift, the experimental τ_{2R} increases by ~20% per hydrogen bond when the density is varied at a constant supercritical temperature.

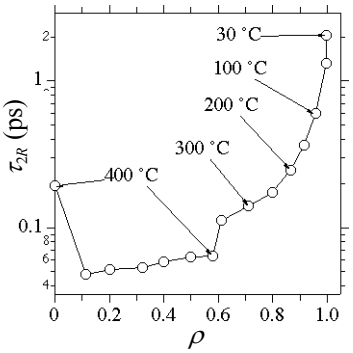

Figure 1. The reorientational correlation time τ_{2R} of heavy water as a function of density ρ.

The angular momentum correlation time τ_J can also be determined from T_1 of light water (H_2O). It is then found that τ_{2R} is comparable to or smaller than τ_J over the entire range of the supercritical conditions examined. In this case, the reorientational relaxation is not diffusive and that the inertial effect is operative. Furthermore, the ratios of τ_{2R} and t_J of D_2O to those of H_2O in the supercritical conditions are ~1.3 and are close to the square root of the ratio of the moment of inertia. Since the viscosity is experimentally coincident within ~5% between H_2O and D_2O in the supercritical conditions, the τ_{2R} difference between H_2O and D_2O reflects the inertial effects in the reorientational relaxation. At the ambient condition of ρ = 1.0 and 30 ºC, on the other hand, since the angular momentum relaxation was found to be faster than the reorientational relaxation by orders of magnitude, the rotational diffusion limit is realized.

In order to obtain quantitative insights into a reaction dynamics in supercritical water, it is often necessary to estimate the lifetime of the hydration structure around the reactive species. According to the previously accumulated data concerning the rotational dynamics of solutions at ambient conditions, it is natural to consider for both ionic and nonpolar solutes that when a super- or subcritical condition is realized, the reorientational relaxation of a water molecule around the solute deviates from that in the pure solvent by a factor of less than ~2. Thus, τ_{2R} determined in the present work serves as the characteristic time for the orientational part of a dynamical process in super- and subcritical water.